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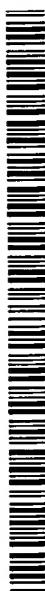
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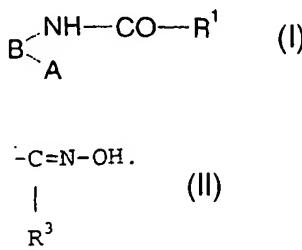
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A1 (54) Title: USE OF TRANSITION METAL COMPLEXES WITH NITROGEN-CONTAINING POLYDENTATE LIGANDS AS A BLEACHING CATALYST AND BLEACHING AGENT COMPOSITION

WO 2004/000986



(57) Abstract: Transition metal complexes are used as bleaching catalysts for peroxy compounds. Transition metal complexes to be used according to the invention contain a ligand of the general formula (I) wherein B is a bridge member, such as o-phenylene or pyridine-2,6-diyl, and A represents the group -NH-CO-R₁ or formula (II).

Use of transition metal complexes with nitrogen-containing polydentate ligands as a bleaching catalyst and bleaching agent composition

Description

5 The invention relates to the use of transition metal complexes with nitrogen-containing polydentate ligands as a bleaching catalyst and to bleaching agent compositions comprising such a bleaching catalyst. The activity of peroxy compounds in washing, bleaching and cleaning
10 processes at low temperature is increased by the transition metal complexes to be used according to the invention.

Inorganic peroxy compounds, in particular hydrogen peroxide and compounds which liberate hydrogen peroxide, such as sodium perborate monohydrate, sodium perborate tetrahydrate
15 and sodium percarbonate, have been employed for a long times as oxidizing agents in bleaching, washing and cleaning processes. Sufficiently rapid bleaching of soiled textiles requires a temperature of at least 80°C.

The oxidizing action of inorganic peroxygen compounds at
20 reduced temperature can be improved by co-using so-called bleaching activators. Bleaching activators are, in particular, N- and O-acyl compounds, for example polyacylated alkylenediamines, such as tetraacetylenediamine (TAED), acetylated glycolurils,
25 N-acetylated hydantoins, diketopiperazines, carboxylic acid anhydrides, carboxylic acid esters, such as, in particular, sodium nonanoyloxy-benzenesulfonate (NOBS), and acylated sugar derivatives.

By using a combination of a peroxy compound and an
30 activator, bleaching can be carried out at about 60°C instead of above 80°C without a loss in activity.

In efforts to be able to carry out washing and bleaching below 60°C, the use of transition metal complexes, in particular complexes of manganese, iron, cobalt and copper with at least one polydentate organic ligand, in particular 5 nitrogen-containing ligands, has been described in many documents.

Reference is made by way of example to the complexes described in the following documents: EP 0 544 490, WO 98/54283, WO 00/12808, WO 00/60043, WO 00/52124, EP 0 392 10 592, WO 99/64156 and WO 00/12667.

Although numerous different transition metal complexes are thus known for the use aimed for, they only partly meet some of the expectations imposed on them.

Thus, if the reactivity is too high there is the risk of a 15 change in colour of dyed textiles, and in the extreme case oxidative damage to the fibres. Furthermore, some complexes decompose the peroxygen compound without a bleaching action, are insufficiently stable to hydrolysis or are susceptible to oxidation.

20 The doctrine of WO 00/32731 is bleaching catalysts with di(2-pyridyl)methylamine organic nitrogen-containing ligand. This catalyst is suitable for increasing the oxidizing and bleaching action of hydrogen peroxide. A further increase is achieved by combination of such a 25 bleaching catalyst with a so-called activator which can form a peroxy carboxylic acid in the presence of a source of hydrogen peroxide. As has been shown in practice, different property profiles of bleaching catalysts which the products known to date do not achieve in all points are required in 30 washing, bleaching and cleaning compositions.

The international application WO 98/03263 discloses homogeneous oxidation catalysts, these being transition metal complexes with a macrocyclic ligand. The ligand

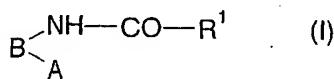
includes four donor atoms, such as nitrogen, usually in the form of amides, so that the ligand is a tetraamide. Further similar macrocyclic ligands and chelate complexes are the doctrine of WO 99/64156, where the ligand can contain four
5 amidic or also two aminic and two amidic nitrogen atoms. Such ligands are indeed stable to oxidation, but the activity as a bleaching catalyst leaves something to be desired.

The object of the present invention is accordingly to
10 provide further transition metal complexes with at least one nitrogen-containing polydentate ligand which are suitable as a bleaching catalyst for activation of a peroxy compound and preferably also oxygen.

It has been found that transition metal complexes with a
15 transition metal from the series consisting of manganese, iron, cobalt or copper are very active and gentle bleaching catalysts if these contain at least one nitrogen-containing polydentate ligand of the general formula (I) according to the claims.

20

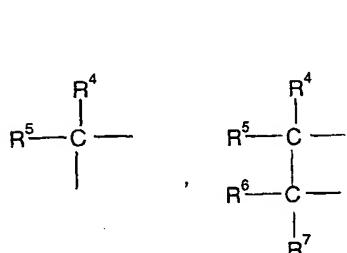
The invention thus provides the use of a transition metal complex with at least one nitrogen-containing polydentate ligand as a bleaching catalyst for activation of a peroxy compound or of oxygen, wherein
25 the complex is mono- or polynuclear, the transition metal (M) is manganese, iron, cobalt or copper and the nitrogen-containing polydentate ligand (L), at least one of which is present, has the general formula (I)



wherein A represents either the group $-\text{NH}-\text{CO}-\text{R}^2$ or the group $-\text{C}=\text{N}-\text{OZ}$,

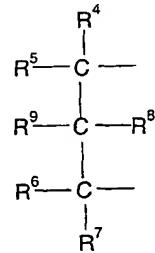


the bridge member B is chosen from the series consisting
5 of

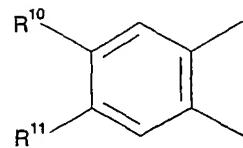


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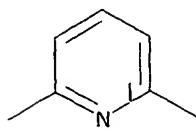
(B1)



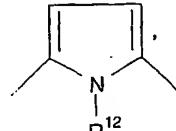
(B2)



(B3)



(B4)



(B5)

wherein R^4 to R^7 independently of one another represent a radical from the series consisting of H, arylalkyl, 10 aryl, heteroaryl,

wherein R^4 with R^5 or/and R^6 with R^7 or R^4 with R^6

together with the atom(s) carrying them can form a five- to seven-membered, in particular five- or six-membered cycloaliphatic or O- or N-heterocyclic ring, which can 15 also contain a double bond,

and wherein the structural elements of the general formulae (B0) to (B5) have a total of 2 to 20 C atoms, R^8 and R^9 independently of one another can represent a radical from the series consisting of H, methyl or together can represent carbonyl oxygen,

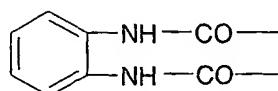
R^{10} and R^{11} independently of one another can represent a radical from the series consisting of H, ($\text{C}_1\text{-}\text{C}_4$)alkyl,

halogen or together can represent a fused-on aromatic ring

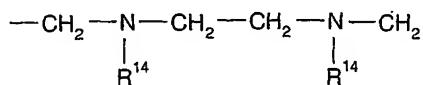
and R¹² can represent H or methyl,

the radicals R¹ and R² independently of one another can represent a radical from the series consisting of -COOH, -CONH₂, -CONHR¹³, C(CH₃)₂OH, 2-pyridyl, 1,3-oxazolin-2-yl, imidazol-2-yl or R¹-R² together can represent the radical

5



or



10

wherein R¹³ can be chosen from the series consisting of linear, branched or cyclic alkyl, aryl, heteroaryl, in particular 2-pyridyl, 1,3-oxazolin-2-yl and imidazol-2-yl and heteroalkylmethyl,

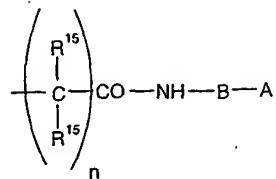
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R¹⁴ can be chosen from the series consisting of substituted or unsubstituted, linear, branched or cyclic alkyl, benzyl, aryl, heteroaryl, heteroarylalkyl, and R³ represents a radical from the series consisting of alkyl, aryl, heteroaryl, arylalkyl, heteroarylalkyl and

20

Z represents H, alkyl, aryl, dialkylaminoethyl, heteroaryl,

and in the case of the oximes R¹ additionally can represent the radical



wherein n is 0 or 1, R^{15} H or alkyl, and the group $R^{15}-C-R^{15}$ can be cycloalkyl.

5 The subclaims relate to preferred embodiments of the use according to the invention.

The present invention also provides the bleaching agent composition defined in the claims, which comprises a peroxy compound, in particular a source of hydrogen peroxide, and 10 a transition metal complex to be used according to the invention in an amount effective for activation. The subclaims of the bleaching agent composition relate to preferred embodiments thereof.

The transition metal complex to be used according to the 15 invention can be mono- or polynuclear and contains as the transition metal one from the series consisting of manganese in the valency level II to IV, iron in the valency level II or III, cobalt in the valency level II or III and copper in the valency level I or II. Depending on 20 the number of heteroatoms capable of ligand formation and their steric alignment in the ligand L, the complex can contain one or more transition metal atoms, preferably one or two metal atoms of the same type. In general the complex has the general formula

25 $[L_m M_n X_o] Y_p$

In this formula, L denotes the ligand to be used according to the invention, M denotes a transition metal atom from the abovementioned series, X denotes a coordinating neutral or mono- or polyvalent ligand for saturation of the ligand sphere and Y denotes a non-coordinating counter-ion, which can be anionic or, if the sum of anionic ligands X and 5 ionic substituents in the ligand L exceeds the sum of the valency of the metal atoms M, can also be cationic. The index m represents an integer in the range from 1 to 4, in particular 1 or 2, the index n represents an integer, 10 preferably 1 or 2, the index o represents zero or an integer in the range from 1 to 8 and the index p represents zero or an integer in order to achieve a complete charge compensation. Y can also be a substituent, such as 15 carboxylate or sulfonate, in the ligand.

The polydentate ligand L to be used according to the invention has the structure according to the general formula (I) already shown. According to a preferred embodiment, the complexes are cobalt complexes with the 20 ligand B(NH-CO-R¹)₂, wherein, particularly preferably, B represents optionally substituted ortho-phenylene and/or R¹ represents a radical from the series consisting of COOH, CONHR', C(CH₃)₂OH where R' is H, (C₁-C₄)-alkyl or substituted alkyl and 2-pyridyl.

25 The bleaching activators to be used according to the invention can in some cases also be macrocyclic, but the ligands differ from the ligands according to WO 98/03263 and WO 99/64156 by at least one feature.

Ligands of preferred bleaching activators are open-chain, 30 that is to say not macrocyclic. Several of these substances are more easily obtainable than the macrocyclic ligands which are already known. Surprisingly, the substances of sometimes simple structure with oxamic acid or oxamide structural elements show a surprisingly good bleaching- 35 activating action. Apart from on the ligand structure and

on the metal atom of the complex, the action also depends in part on the coloured substance to be bleached.

A new genus of active transition metal complexes contain a chelate ligand with four nitrogen donor atoms, two of which
5 have an amide structure and two N atoms of which are the constituent of an N-heterocyclic ring.

Finally, ligands with two amide groups and two oxime groups are interesting compounds for complexing of Mn, Fe, Co and Cu for the purpose of obtaining active bleaching
10 activators.

The cyclic bridge members B can also have functional or non-functional substituents, for example OH, NH₂, COOH, SO₃H, COOMe, SO₃Me, wherein Me represents an alkali metal,
15 N⁺(C₁-C₄-alkyl)₄, F, Cl, alkoxy, in particular (C₁-C₄)alkoxy, alkyl, in particular (C₁-C₄)alkyl, phenyl, benzyl, pyridyl, 2-pyridylmethyl.

The radicals R¹ and R² in the ligand L can be identical or
20 different and represent H, linear, cyclic or branched alkyl or heteroalkyl, aryl, heteroaryl, arylalkyl and heteroarylalkyl. Examples are methyl, ethyl, i-propyl, tert-butyl, benzyl, phenyl, pyridyl, in particular 2-pyridyl, 1,3-oxazolin-2-yl, 1,3-oxazolin-2-methyl and 2-pyridylmethyl.

The radical R³ in the ligand L can be aryl, heteroaryl; alkoxy, aryloxy, heteroaryl, alkyl and arylalkyl. The examples mentioned above for R¹ and R² also apply here. If
30 R³ represents alkoxy or aryloxy, it is preferably methoxy,

ethoxy, 2-hydroxyethoxy, 2-aminoethoxy, 2-N,N-di(C₁-C₄)alkylaminoethoxy and phenoxy.

Both the radicals R¹ to R³ and bridge members (B1 to B5) 5 can have one or more functional or non-functional substituents. These are those substituents such as have already been disclosed in connection with the description of the bridge member B. According to particularly preferred embodiments, the heterocyclic or heteroaromatic ring 10 systems bonded to the bridge member B contain one or more linear or branched (C₁-C₄)alkyl groups, in particular methyl, isopropyl and tert-butyl, and furthermore phenyl, benzyl, 2-pyridylmethyl or -ethyl or 4-imidazolylmethyl or -ethyl.

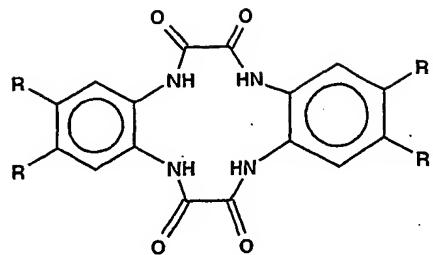
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According to a further preferred embodiment, one or more radicals from the series consisting of R¹ to R¹⁵ or the nitrogen-containing ring systems formed therefrom contain hydrophilic substituents in order to increase the 20 solubility of the complex. Examples of these are salt-forming functional substituents and hydroxyalkoxy groupings, which additionally can also contain one or more ether bridges.

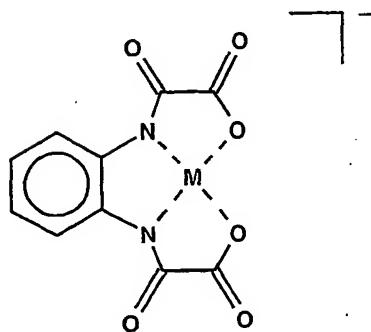
25 The chemical name for some examples of suitable ligands and the formulae of some complexes containing them follow below:

5,8,13,16-tetrahydro-5,8,13;16-tetraaza-dibenzo[a,g]cyclododecene-6,7,14,15-tetraone (TTBP)

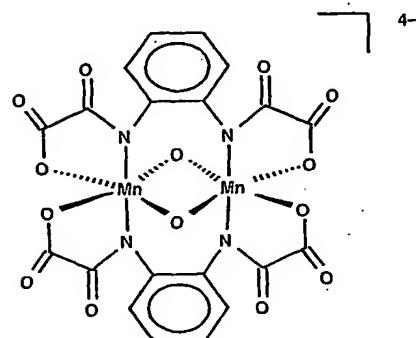
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1,2-phenylene-bisoxamic acid (OPBA)



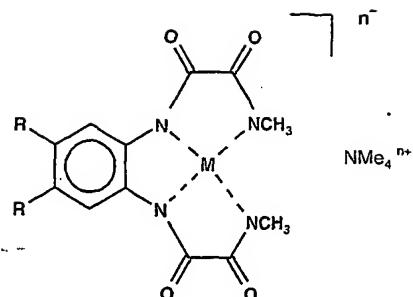
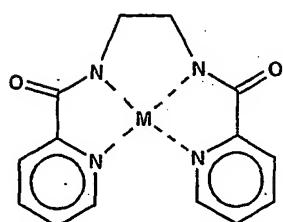
Mn complex of 1,2-phenylene-bisoxamic acid



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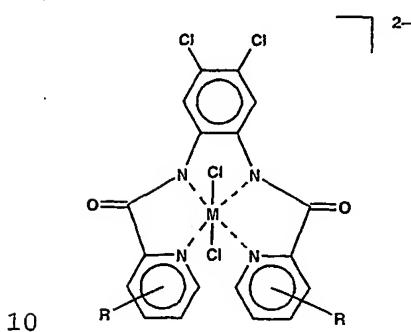
N-methyl-N'-(2-(methylaminooxalylamino)phenyl)oxalamide
(PBOMA)N-[4,5-dichloro-2-(methylaminooxalylamino)phenyl]-N'-
methyloxalamide (for R = Cl)

11

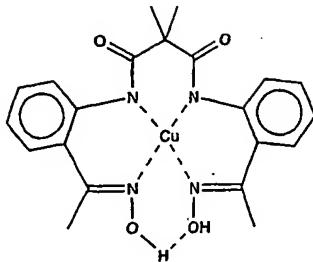
*N,N'-bis(pyridine-2-carboxamido)-1,2-ethane (BPEN)*

5

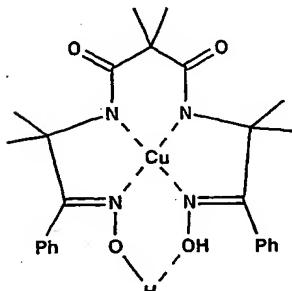
1,2-bis(pyridine-2-carboxamido)-4,5-dichlorobenzene (PCADB)
 1,2-bis(4-*tert*-butylpyridine-2-carboxamido)-4,5-dichlorobenzene (for R = tBu)

*N,N'-bis[2-(1-hydroxyiminoethyl)phenyl]-dimethylmalonodiamide*

12.



N,N'-bis [2-(2-methyl-1-oxo-1-phenyl)propyl]-
dimethylmalonodiamide



5

Apart from the ligand L, the catalyst can additionally contain coordinating co-ligands X. X here can be a mono-, di- or trivalent anion or a neutral molecule, which can be coordinated with the transition metal in a mono-, bi- or tridentate manner. The co-ligand is preferably the following groupings: OH⁻, O²⁻, NO₃⁻, PO₄³⁻, CN⁻, SCN⁻, HSO₄⁻, SO₄²⁻, Cl⁻, Br⁻, F⁻, ClO₄⁻, OCN⁻, HCO₃⁻, RS⁻, CO₃²⁻, SO₃²⁻, RSO₃⁻, S₂O₆²⁻, RCO₂⁻; H₂O, ROH, CH₃CN, NRR'R''.

15

The counter-ion Y of the complex to be used can be anionic or cationic, wherein the number p is chosen such that complete charge compensation is achieved. The counter-ion can preferably have the following meaning: F⁻, Cl⁻, Br⁻, I⁻, NO₃⁻, RSO₃⁻ (R e.g. preferably CF₃), ClO₄⁻, RCO₂⁻, PO₄³⁻,

HPO_4^{2-} , H_2PO_4^- , SO_4^{2-} , HSO_4^- , CO_3^{2-} , HCO_3^- , BF_4^- , PF_6^- , SO_3^{2-} ; Li^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Ba^{2+} .

The bleaching catalysts to be used according to the

5 invention activate elemental oxygen and peroxy compounds. Peroxy compounds are to be understood as meaning, in particular, hydrogen peroxide, compounds which liberate hydrogen peroxide, such as, in particular, sodium perborate monohydrate, sodium perborate tetrahydrate and sodium

10 percarbonate, perphosphates and persulfates, peroxydicarboxylic acids and salts thereof and peroxydicarboxylic acid bleaching precursors, so-called activators, and mixtures of such substances. Suitable peroxydicarboxylic acids can be aliphatic or aromatic in

15 nature and contain one or more peroxydicarboxylic acid groups. Aliphatic peroxydicarboxylic acids usually contain 1 to 20 C atoms, preferably 1 to 12 C atoms, and the particularly preferred peroxydicarboxylic acid is peroxyacetic acid. Among the peroxydicarboxylic acids with 2

20 peroxydicarboxylic acid groups, those having 4 to 18 C atoms are preferred; examples are diperoxyadipic acid, diperoxyazelaic acid, diperoxylauric acid and diperoxydodecanedioic acid, as well as salts of the acids mentioned, for example magnesium salts. Among the aromatic

25 peroxydicarboxylic acids there are, in particular, peroxybenzoic acid, m-chlorobenzoic acid, p-sulfonatoperoxybenzoic acid, diperoxyisophthalic acid, phthalimidopercaproic acid, 4,4'-sulfonyl-diperoxybenzoic acid and magnesium salts of these acids.

30

The peroxydicarboxylic acids can also be formed in situ under the use conditions, and in particular from so-called activators, which are in general O-acyl compounds and N-acyl compounds. Such compounds form the corresponding

peroxycarboxylic acid under perhydrolysis conditions in the presence of hydrogen peroxide or a source of hydrogen peroxide. Activators which are particularly preferably to be used are: N,N,N'N'-tetraacetyl ethylenediamine (TAED), Na

5 1-methyl-2-benzoyloxybenzene-4-sulfonate, Na nonanoyloxybenzenesulfonate (NOBS), 2-(N,N,N-trimethylammonium)ethyl-sodium 4-sulfophenylcarbonate chloride (SPCC), pentaacetylglucose, phthalic anhydride.

10 For activation of peroxy compounds, the transition metal complexes to be used according to the invention are in general employed in an amount of about 0.0001 to 50 wt.%, in particular 0.01 to 20 wt.% and particularly preferably 0.01 to 1 wt.%, based on the peroxy compounds.

15

Bleaching agent compositions according to the invention comprise at least one peroxy compound and a transition metal complex to be used according to the invention in an active amount. Such compositions expediently comprise 0.001
20 to 50 wt.%, in particular 0.01 to 20 wt.% and particularly preferably 0.01 to 1 wt.% of a transition metal complex with a ligand according to the invention, based on the content of peroxy compounds or precursor of one.

25 Bleaching agent compositions according to the invention expediently additionally comprise one or more surfactants from the series consisting of anionic, cationic, zwitterionic and nonionic surfactants, in particular surfactants such as are used in conventional washing, bleaching and
30 cleaning compositions. Bleaching agent compositions according to the invention can furthermore also comprise organic and/or inorganic builders, such as zeolites. Further constituents can be those such as are used in

conventional washing, bleaching and cleaning compositions, including enzymes, pH regulators and conventional alkali metal carriers, such as alkali metal silicate and alkali metal carbonates.

5 **Examples**

Example 1:

Preparation of the dibenzotetramide 5,8,13,16-tetrahydro-5,8,13,16-tetraaza-dibenzo[a,g]cyclododecene-6,7,14,15-tetraone (TTBP)

10 Ligand: A solution of 5.52 g (17.9 mmol) diethyl 1,2-phenylene-dioxamate (preparation in accordance with: J. Am. Chem. Soc. 1993, 115(15), 6738) and 1.94 g (17.9 mmol) 1,2-phenylenediamine in 250 ml toluene was heated under reflux for 8 hours. The product was then filtered off and dried in
15 vacuo at 50°C. Yield: 29% (pale green solid).

M complex (M = Fe, Cu, Mn, Co): 500 mg (1.54 mmol) of ligand were dissolved in 50 ml THF under argon and the solution was then cooled to -100°C. 4.2 ml (6.17 mmol) n-
20 butyllithium (15 per cent in pentane) were added all at once by means of a disposable syringe and, after 15 minutes, 195 mg (1.54 mmol) anhydrous iron(II) chloride were added. The reaction mixture was warmed to room temperature and stirred at this temperature for 22 hours.
25 Atmospheric oxygen was then passed through the solution in the course of 2 hours. The red-brown solid was filtered off and dried at 50°C in vacuo. Yield: 96%

Analogously, the Mn complex was prepared with anhydrous MnCl₂ (42%, red-brown solid), the Cu complex with anhydrous CuCl₂ (70%, dark brown solid) and the Co complex with anhydrous CoCl₂ (83%, dark red solid).

Example 2:

Preparation of N-methyl-N'-(2-(methylamino)oxalylamino)-phenyl]oxalamide (PBOMA)

N,N'-1,2-Phenylene-bis(oxamic acid ethyl ester)

5 8.40 g (60.0 mmol) ethoxalyl chloride were added dropwise to a solution of 3.30 g (30.0 mmol) 1,2-phenylenediamine in 150 ml tetrahydrofuran analogously to the instructions in *J. Am. Chem. Soc.* 1993, 115(15), 6738. The solution was heated under reflux for 0.5 hour and solid constituents
10 were then filtered off. After distillation of the solvent, a little water was added to the oily residue, a colourless solid precipitating out. This was filtered off, washed with water and dried in vacuo. (Yield: 97%)

15 Reaction of the diester with methylamine

8.24 g (87.5 mmol) methylamine (33% in methanol) were added dropwise to a solution of 9.00 g (29.2 mmol) of the diethyl ester in 50 ml ethanol analogously to the instructions in *J. Chem. Soc. Dalton Trans.* 1997, 745 at room temperature
20 and the reaction solution was then stirred vigorously for 0.5 hour at 65°C. The colourless solid was filtered off, washed with a little cold methanol and methyl tert-butyl ether and dried in vacuo. (Yield: 82%)

25 Co complex of PBOMA:

2.62 g (7.18 mmol) cobalt(II) perchlorate dihydrate, which were dissolved in a little methanol beforehand, were added to 2.00 g (7.18 mmol) of the bisamide PBOMA and 11.0 g (30.2 mmol) tetramethylammonium hydroxide in 10 ml
30 methanol. A pale red solid precipitated out. This was filtered off and dried. (Yield: 84%)

Examples 3 to 8

The complexes of examples 1 and 2 and complexes prepared in an analogous manner or a manner known from the literature 5 were investigated for their catalytic action by means of the Morin test and in some cases by means of a washing test.

Morin test: A sodium perborate monohydrate solution, a methanolic solution of tetraacetyl ethylenediamine and a 10 dilute solution of the combination to be investigated are added to an aqueous Morin solution.

After intensive mixing, the extinction/transmission is measured at 400 nm after 30 minutes at 30°C. The blank value is measured in the absence of the combination to be 15 investigated.

Washing test: Laboratory washing apparatus type ATLAS LAUNDER-O-METER

Temperature: 30 °C

20 Washing time: 30 minutes

Water hardness: 14°d

Staining: tea, in some cases also grass on cotton

Detergent recipe:

12.2% anionic surfactant

25 7.7% nonionic surfactant

2.0% soap

34.8% zeolite A

4.2% polycarboxylate

0.5% phosphonic acid

30 4.1% corrosion inhibitor

1.1% magnesium silicate

1.1% greying inhibitor (CMC)

2.2% sodium sulfate

4.1% sodium citrate

Bleaching component:

5 17% sodium percarbonate

5% activator TAED

Metal complex: 2,400 ppm

Detergent concentration: 5 g/l

As a comparison, the base recipe plus percarbonate/TAED,
10 but without a metal complex (= catalyst) was always run
but without a metal complex (= catalyst) was always run
(CE1). This change in reflection compared with the starting
fabrics is subtracted from the change in reflection
achieved with percarbonate/TAED/bleaching catalyst.

The results follow from the table:

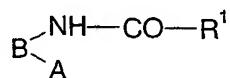
Table:

No.	Complex			Morin test transmission	Washing test (Δ R)
	M	L	X or Y		
3	Co	TTBP		94.8	0.2
4	Co	PBOMA	$Y=N(CH_3)_4^+$	94.8	1.9
5a	Co	OPBA		13	1.5
5b	Cu	OPBA		13.8	n.d.
5c	Fe	OPBA		5.8	n.d.
6	Mn	OPBA	$X=(\mu O)_2$ $Y=(Na^+)_4$	4.2	n.d.
7	Mn	BPEN		8	n.d.
8a	Co	PCADB	$X=(Cl^-)_2$ $Y=(Na^+)_4$	6.2	n.d.
8b	Fe	PCADB	$X=(Cl^-)_2$ $Y=(Na^+)_4$	46	n.d.

The test results show that the catalysts according to the invention, in particular cobalt complexes, lead to a high
5 increase in the activity of the peroxyacetic acid formed in situ from an activator (TAED) and perborate.

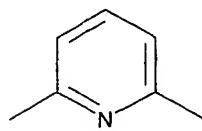
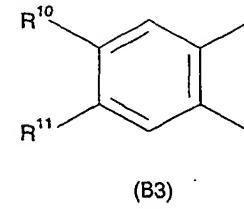
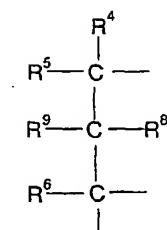
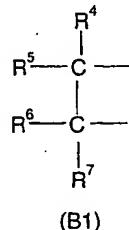
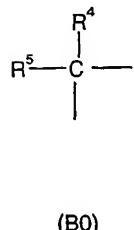
Patent claims:

1. Use of a transition metal complex with at least one nitrogen-containing polydentate ligand as a bleaching catalyst for activation of a peroxy compound or of
 5 oxygen, wherein
 the complex is mono- or polynuclear, the transition metal (M) is manganese, iron, cobalt or copper and the nitrogen-containing polydentate ligand (L), at least one of which is present, has the general formula (I)



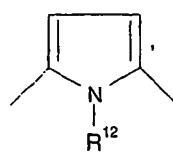
10 wherein A represents either the group $-\text{NH}-\text{CO}-\text{R}^2$ or the group $-\text{C}=\text{N}-\text{OZ}$,
 $\begin{array}{c} | \\ \text{R}^3 \end{array}$

the bridge member B is chosen from the series consisting of



15

(B4)



(B5)

wherein R⁴ to R⁷ independently of one another represent a radical from the series consisting of H, arylalkyl, aryl, heteroaryl,

wherein R⁴ with R⁵ or/and R⁶ with R⁷ or R⁴ with R⁶

5 together with the atom(s) carrying them can form a five- to seven-membered cycloaliphatic or O- or N-heterocyclic ring, which can also contain a double bond,

and wherein the structural elements of the general formulae (B0) to (B5) have a total of 2 to 20 C atoms,

10 R⁸ and R⁹ independently of one another can represent a radical from the series consisting of H, methyl or together can represent carbonyl oxygen,

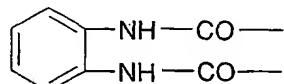
R¹⁰ and R¹¹ independently of one another can represent a radical from the series consisting of H, (C₁-C₄)alkyl,

15 halogen or together can represent a fused-on aromatic ring

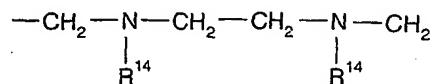
and R¹² can represent H or methyl,

the radicals R¹ and R² independently of one another can represent a radical from the series consisting of -COOH,

20 -CONH₂, -CONHR¹³, C(CH₃)₂OH, 2-pyridyl, 1,3-oxazolin-2-yl, imidazol-2-yl or R¹-R² together can represent the radical



or



25

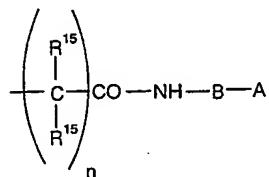
wherein R¹³ can be chosen from the series consisting of linear, branched or cyclic alkyl, aryl, heteroaryl, in particular 2-pyridyl, 1,3-oxazolin-2-yl and imidazol-2-yl and heteroalkylmethyl,

30 R¹⁴ can be chosen from the series consisting of substituted or unsubstituted, linear, branched or cyclic

alkyl, benzyl, aryl, heteroaryl, heteroaryl methyl, and R³ represents a radical from the series consisting of alkyl, aryl, heteroaryl, arylalkyl, heteroarylalkyl and Z represents H, alkyl, aryl, dialkylaminoethyl,

5 heteroaryl

and in the case of the oximes R¹ additionally can represent the radical

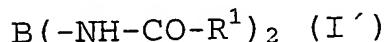


wherein n is 0 or 1, R¹⁵ can be H or alkyl and R¹⁵-C-R¹⁵ can be cycloalkyl.

10 2. Use according to claim 1,

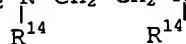
characterized in that

the ligand L has the general formula



15 wherein B represents unsubstituted or substituted ortho-phenylene, wherein the substituents can be bonded in particular in the 4,5-position and can be Cl, F or CH₃, and/or R¹ is chosen from the series consisting of COOH, CO-NH-CH₃, C(CH₃)₂OH, 2-pyridyl, 1,3-oxazolin-2-yl and imidazol-2-yl or R¹ represents a radical from the series consisting of phenylenediamine-N,N'-dicarbonyl or

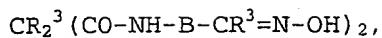
20 CH₂-N-CH₂-CH₂-N-CH₂-, where R¹⁴ is -CH₂-COOH.



3. Use according to claim 1 or 2,

25 characterized in that

the ligand L in the diamide-dioxime corresponds to the general formula



wherein B represents substituted ortho-phenylene and R³ represents methyl.

4. Use according to one of claims 1 to 3

5 characterized in that

the complex has the general formula [L_mM_nX_o]Y_p,

wherein L denotes a ligand according to one of claims 1 to 6

10 M denotes a transition metal from the series consisting of Mn(II) to Mn(IV), Fe(II), Fe(III), Co(II), Co(III),

Cu(I) and Cu(II), in particular Co(II) or Co(III),

15 X denotes a coordinating neutral or charged mono- or polyvalent ligand for saturation of the ligand sphere and

Y denotes a non-coordinating counter-ion which can be anionic or, if the sum of anionic substituents in the ligand L exceeds the sum of the valency of the metal atoms M, can also be cationic,

20 m denotes an integer in the range from 1 to 4, in particular 1 or 2,

n denotes the number 1 or 2,

o denotes zero or an integer in the range from 1 to 8 and

25 p denotes zero or an integer in the range from 1 to 8, in order to achieve complete charge compensation.

5. Use according to claim 4,

characterized in that,

a complex of the general formula [LMX_o]Y_p or [L₂M₂X_o]Y_p,

wherein the bridge member B of the ligand B(NH-CO-R¹)₂

30 denotes ortho-phenylene or 4,5-dichlorophenylene and R¹

denotes a radical from the series consisting of COOH, CONHCH₃, C(CH₃)₂OH and 2-pyridyl, is employed.

6. Use according to one of claims 1 to 5,

characterized in that

hydrogen peroxide or a peroxy carboxylic acid having 2 to 18 C atoms, which can also have been formed in situ from a source of hydrogen peroxide and an activator from the series consisting of O-acyl or N-acyl compounds, is
5 activated.

7. Use according to one of claims 1 to 6

characterized in that

the transition metal complex is employed in an amount of 0.0001 to 50 wt.%, based on the peroxy compound.

10 8. Bleaching agent composition comprising a peroxy compound and a transition metal complex in an amount effective for activation of the peroxy compound,
characterized in that
it comprises a transition metal complex according to one
15 of claims 1 to 5.

9. Bleaching agent composition according to claim 8,

characterized in that

the peroxy compound is chosen from the series consisting of hydrogen peroxide, a source of hydrogen peroxide, in particular an alkali metal perborate monohydrate tetrahydrate or alkali metal percarbonate, a peroxy carboxylic acid having 2 to 18 C atoms or a combination of a source of hydrogen peroxide and a peroxy carboxylic acid precursor, in particular an O-acyl or N-acyl compound, or from mixtures thereof.
25

10. Bleaching agent composition according to claim 8 or 9,

characterized in that

it additionally comprises one or more surfactants, in particular wash-active surfactants.

30 11. Bleaching agent composition according to one of claims 8 to 10,
characterized in that

it additionally comprises builders, in particular zeolites.

12. Bleaching agent composition according to claim 10 or
11,

5 characterized in that

it is a constituent of a washing, bleaching or cleaning composition comprising one or more surfactants and one or more builders.

13. Bleaching agent composition according to one of claims
10 8 to 12,

characterized in that

it comprises 0,0001 to 50 wt.%, in particular 0.01 to 20 wt.% of a transition metal complex according to one of claims 1 to 7, based on the content of peroxy compound or precursor thereof.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 03/05674

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C11D3/39

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT
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A	WO 98 03263 A (CARNEGIE MELLON UNIVERSITY (US)) 29 January 1998 (1998-01-29) cited in the application the whole document	1-13
A	US 2002/058598 A1 (AVILA DAVID VICTOR) 16 May 2002 (2002-05-16) the whole document	1-13
A	US 2001/003737 A1 (REINEHR DIETER ET AL) 14 June 2001 (2001-06-14) the whole document	1-13
A	US 5 969 171 A (NESTLER BERND) 19 October 1999 (1999-10-19) the whole document	1-13
		-/-

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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& document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
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3 September 2003

11/09/2003

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Diebold, A.

INTERNATIONAL SEARCH REPORT

Internal Application No
PCT/EP 03/05674

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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P,A	US 2002/165110 A1 (REINHARDT GERD ET AL) 7 November 2002 (2002-11-07) the whole document -----	1-13
P,A	US 2002/134965 A1 (DANJO HIROSHI) 26 September 2002 (2002-09-26) the whole document -----	1-13
A	WO 02 16330 A (UNILEVER PLC (GB); UNILEVER NV (NL); HINDUSTAN LEVER LIMITED (IN)) 28 February 2002 (2002-02-28) the whole document -----	1-13

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Form PCT/ISA/210 (patent family annex) (July 1992)

BNSDOCID: <WO_____2004000986A1_I_>

INTERNATIONAL SEARCH REPORT

Information on patent family members

Internal Application No
PCT/EP 03/05674

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US 6241779	B1	CN DE DK EP JP NO NZ PL RU WO AP AT AU AU BR CA CN DE DE EP ES JP NO NZ PL RU WO US	1230980 A 69719337 D1 923635 T3 0923635 A2 2000515194 T 990267 A 333795 A 331352 A1 2193049 C2 9803626 A2 1013 A 225844 T 730906 B2 3665597 A 9710538 A 2261228 A1 1230979 A 69716275 D1 69716275 T2 0918840 A1 2186906 T3 2001503073 T 990266 A 333796 A 331316 A1 2193050 C2 9803625 A1 6099586 A	06-10-1999 03-04-2003 23-06-2003 23-06-1999 14-11-2000 15-03-1999 28-07-2000 05-07-1999 20-11-2002 29-01-1998 27-09-2001 15-10-2002 15-03-2001 10-02-1998 17-08-1999 29-01-1998 06-10-1999 14-11-2002 10-07-2003 02-06-1999 16-05-2003 06-03-2001 22-03-1999 29-09-2000 05-07-1999 20-11-2002 29-01-1998 08-08-2000
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